

Synthesis and Characterization of $\text{Mn}_{1-x}\text{Mo}_x\text{V}_{2(1-x)}\text{O}_6$ ($0 \leq x \leq 0.5$) and Their Application as the Anode for Li Secondary Battery

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Introduction

Graphite is commonly used as the anode material for Li-ion secondary battery. However, the graphite anode has some problems such as relatively small capacity, low energy density. To overcome these problems, Kim et al. [1] suggested the brannerite-type structure MnV_2O_6 as a new candidate for the anode material.

In this work, we synthesized $\text{Mn}_{1-x}\text{Mo}_x\text{V}_{2(1-x)}\text{O}_6$ ($0 \leq x \leq 0.5$) which have the same to the MnV_2O_6 brannerite-type crystal structure to improve the performances of MnV_2O_6 . In $\text{Mn}_{1-x}\text{Mo}_x\text{V}_{2(1-x)}\text{O}_6$ ($0 \leq x \leq 0.5$), Mn and their vacancies occupy randomly over the original Mn sites, and V and Mo occupy randomly over the original V sites in the MnV_2O_6 [2].

We report the effects of the substitutions of original Mn sites by vacancies and V sites by Mo on electrochemical performance for $\text{Mn}_{1-x}\text{Mo}_x\text{V}_{2(1-x)}\text{O}_6$ ($0 \leq x \leq 0.5$) as the anode material, and also present the mechanism of initial lithiation.

Experimental

Starting materials used were Mn_2O_3 , V_2O_5 and MoO_3 . Stoichiometric mixture of these materials were pressed into a pellet and heated in air using alumina crucible. Intermittent-grindings were performed to ensure complete solid-solid reaction. XRD analysis was used to determine the crystal structure.

The samples for electrochemical measurements were prepared by mixing $\text{Mn}_{1-x}\text{Mo}_x\text{V}_{2(1-x)}\text{O}_6$ ($0 \leq x \leq 0.5$), acetylene black and polytetrafluoroethylene (PTFE) binder (55-40-5 wt%) in an agate mortar and then pressed into a film. The film was then cut into a disk form (5.4 mm diameter, 1 mg weight). Lithium foil of the same area was used as a counter electrode. 1 M LiClO_4 dissolved in EC / DEC (vol ratio = 1:1) was used as the electrolyte.

The electrochemical measurement was carried out galvanostatically at 0.2 mA/cm² at room temperature in a grove box under an argon atmosphere. The cutoff voltage was set at 0.01 V and 2.5 V. To investigate the structural change of active materials during the first discharge, ex-situ XRD measurement were performed at various voltages.

Results and Discussion

From XRD patterns, all the prepared samples had brannerite-type structures similar to MnV_2O_6 .

Fig. 1 shows discharge capacity versus cycle number of Li / $\text{Mn}_{1-x}\text{Mo}_x\text{V}_{2(1-x)}\text{O}_6$ ($x = 0.1, 0.3, 0.5$) cell. All these active materials have large capacity values compared with that of graphite. Large irreversible capacity loss between the first and second cycle, and capacity fading with cycle number can be seen. The performance was improved as the value of x increases.

Fig. 2 shows a typical charge-discharge profile of Li / $\text{Mn}_{0.5}\text{MoVO}_6$ cell at the first and second cycles. XRD of the electrode were measured on each voltage represented by solid symbols on the first discharge curve. Three plateaus are observed on the first discharge at around 0.9 V, 0.65 V and 0.23 V.

Fig. 3 shows XRD patterns of $\text{Mn}_{0.5}\text{MoVO}_6$ at

various fixed voltages. Peaks indicated by the symbol ▼ come from polyethylene film which covered on the surface of electrode to prevent from moisture in air. The figure indicates that $\text{Mn}_{0.5}\text{MoVO}_6$ becomes amorphous along the insertion of lithium ion during the first discharge. New peaks appeared at around 40° and 30° in the case of 0.50 V and they disappeared gradually through the insertion of lithium ion. The total numbers of cations (Li + Mn + V + Mo) equal to those of oxygen at 0.50 V since the number of lithium inserted at the 0.50 V corresponds to around 3.5. Therefore the brannerite structure transforms to amorphous via a kind of NaCl rock-salt structure during the first discharge.

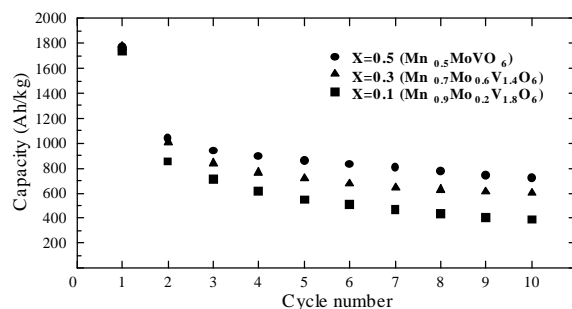


Fig. 1 Discharge capacities versus cycle number

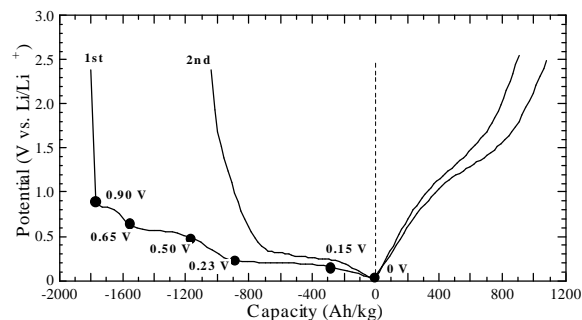


Fig. 2 Typical charge-discharge profile of $\text{Mn}_{0.5}\text{MoVO}_6$.

References

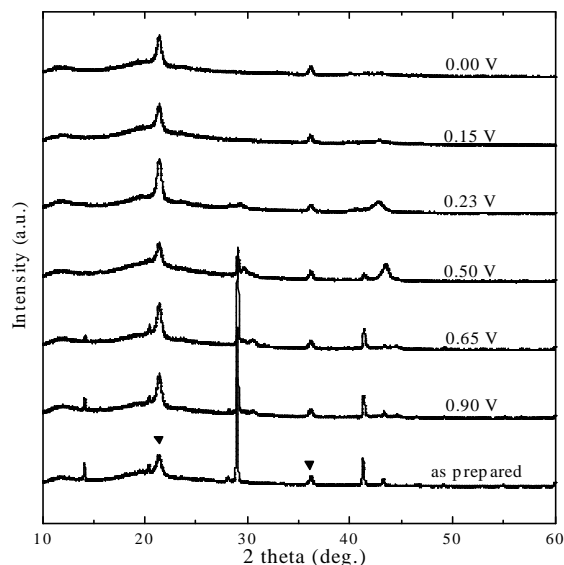


Fig. 3 X-ray diffraction patterns of $\text{Mn}_{0.5}\text{MoVO}_6$ on various voltages.

- 1) S-S. Kim, H. Ikuta and M. Wakihara, *Solid State Ionics*, 139 (2001) 57
- 2) R. Kozłowski, J. Ziolkowski, K. Mocala and J. Haber, *J. Solid State Chem.*, 35 (1980) 1